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IMPROVED CHEMICAL COMPONENTS FOR FORMULATING FIBERGLASS-REINFOR--ETC(U)

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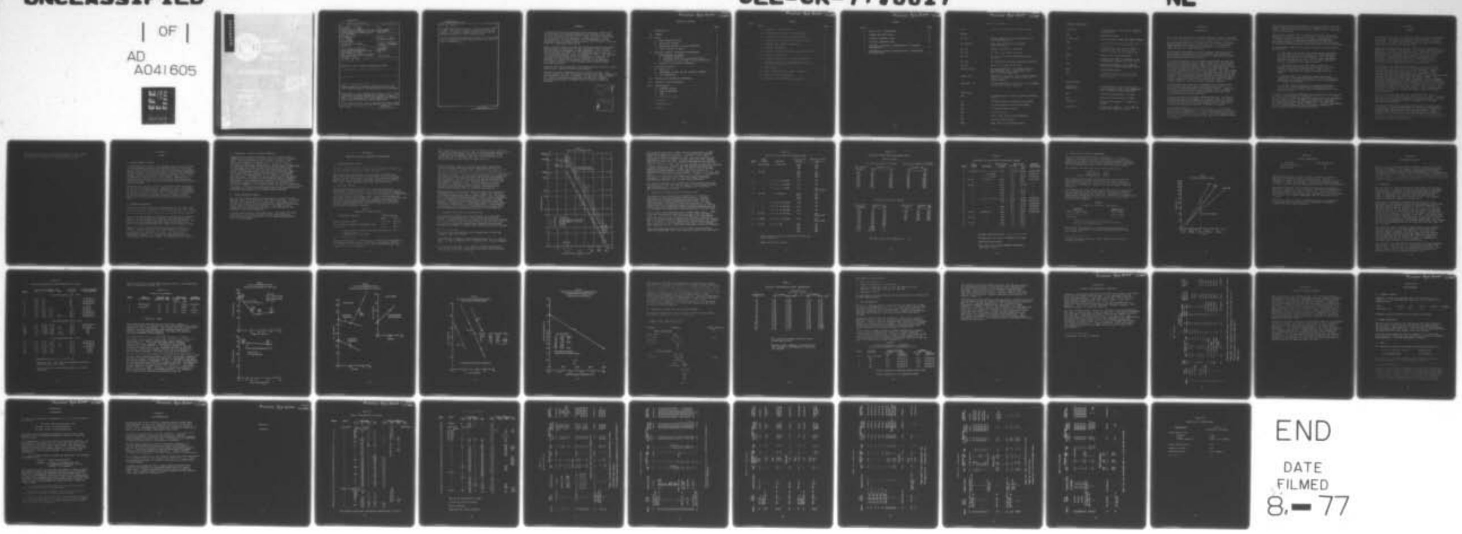

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A stabilized resin was formulated which displayed a shelf life by accelerated test methods substantially in excess of 5 years at 75°F. It was discovered that 2,4-dinitrophenol and p-tolyhydroquinone act synergistically to enhance stabilization.

A new, reliable catalyst system was developed that gives reliable

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cure with adjustable gel times over a temperature range of 40°F to 120°F. The catalyst is cumene hydroperoxide (CHP) and the promoter is a solution of Vanadium Ten Cem (5% metal) and N,N-dimethyl-p-toluidine in a 2.4/2.0 ratio by volume.

The newly developed formulation uses components with longer shelf lives is useable over a wider temperature range, and results in better FRP properties.

ABSTRACT

A stabilized resin was formulated which displayed a shelf life by accelerated test methods substantially in excess of 5 years at 75°F, and had a working life of 5 years at 75°F at which time the resin will still be sprayable in AMSS equipment. It was discovered that 2,4-dinitrophenol and p-toluhydroquinone act synergistically to enhance stabilization, with 600 ppm 2:1 DNP:THQ being the recommended combination.

A new, reliable catalyst system was developed because the present AMSS catalyst system failed to cure stabilized resin suitably. The new system is adaptable to AMSS equipment, gives reliable cure with adjustable gel times over the specified range of 40°F to 120°F, uses less material, and is pumpable at -25°F. The catalyst is cumene hydroperoxide (CHP); the promoter is a solution of Vanadium Ten Cem (5% metal) and N,N-dimethyl-p-toluidine. Equipment to prepare the promoter solution will be necessary. The promoter solution is less hazardous than presently used N,N-dimethylaniline.

Flexural and tensile strength of FRP mats prepared at 40°F to 120°F substantially exceed specified requirements.

Only the peroxidic components pose a stability problem. CHP is more stable and safer than presently used Cadox 40E. Technically, low temperature storage is feasible. If CHP were stored at 60°F for 5 years, deterioration would be less than 10%, however, peroxide manufacturers recommend against extended storage of peroxides.

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GLOSSARY OF TERMS

AMSS	Advanced Multipurpose Surfacing System
Resins	
Rs 50129	Present AMSS resin (PPG Industries, Inc., Fort Washington, PA)
RS 50129(PH)	Resin received from Port Hueneme (mfg. June 1972)
SR 3703	Samples from PPG, as RS 50129
SR 3704	SR 3703, with extra inhibitor
SR 3705	RS 50129 resin with Methylhydroquinone inhibitor
SR 3706	RS 50129 resin with Methylquinone inhibitor
SR 3707	Blend of SR 3705 and SR 3706
Primary Resin	Kirtland AFB resin, 76% ALTEK® 8-52 and 24% DERAKANE® 510, a brominated vinyl ester, 300 ppm added THQ.
ALTEK® 8-52	Isophthalic polyester resin (Alpha Chemical Corp.); formulated from ALTEK 8-60 by adding styrene.
DERAKANE® 510	A brominated vinyl ester resin. (A trademark of The Dow Chemical Company.)
Inhibitors	
THQ	Toluhydroquinone (Eastman Chemical Products Inc.).
DN	2,4-Dinitro-ortho secondary butylphenol
DNP	2,4-Dinitrophenol (Pfaltz and Bauer).
DNC	2,4-Dinitro-ortho cresol
ONP	Orthonitrophenol
PA	Picric Acid (2,4,6-Trinitrophenol).
TBC	Tertiary Butylcatechol
MTBH	Mono tertiary butylhydroquinone

Catalyst Components

CADOX® 40E	A 40% emulsion of BPO (Noury Chemical Corporation).
BPO	Benzoyl Peroxide
S-0046 Green	Color pigmented Cadox 40E (AMSS System)
CHP	Cumene hydroperoxide (Hercules, Inc., or Lucidol Division, Pennwalt Corp.)
DDM	LUPERSOL® DDM, a 60% solution of MEKP in dimethylphthalate (Lucidol Division or Wallace & Tiernan Division, Pennwalt Corp).
MEKP	Methyl ethyl ketone peroxide
V	Vanadium TEN CEM, 5% Vanadium as the neodecanoate (Mooney Chemicals, Inc.).
CoN	Cobalt naphthenate, 6% Co (Nuodex Division of Tenneco Chemicals, Inc.).
DMA	N,N-Dimethylaniline
DMT	N,N-Dimethyl-p-toluidine (Eastman Kodak Co., Mobay Chemical Co., or R.S.A. Corp.).

Miscellaneous

FABMAT® 2418 FABMAT® 4020	Glass composite, woven, roving and chopped strand (Fiber Glass Industries, Inc., Hexcell-Traverno Division).
phr	Parts per hundred parts of resin.
ppm	Parts per million parts of resin.
Promoter K	Kirtland AFB System - 2:1 DMT:V, by volume
Promoter PH	Recommended Promoter - 3:2 V:DMT, by volume; 2:1 V:DMT, by weight

SECTION I

INTRODUCTION

The object of the work is to develop improved chemical components to be used in constructing fiberglass reinforced plastic surfacings for soil. The improved chemical components shall (1) have a minimum shelf stability of 5 years and (2) be usable with basic spray equipment now used by the Marine Corps. The work was funded by the Civil Engineering Laboratory, Port Hueneme, CA under Contract No. N68305-76-C-003.

Marine Corps requirements for rapid response and mobility call for methods by which Marine Corps engineers can upgrade the load-carrying capacity of native soils for temporary but often heavy vehicular and aircraft loads.

A recent development in soil surfacing techniques has been the fiberglass reinforced plastic (FRP) system called the Advanced Multipurpose Surfacing System (AMSS). The system pumps resin, catalyst and promoter through a hand-held spray gun, from which the materials are directed onto and into a fiberglass mat previously placed directly on the soil surface. Two resin hoses, one with added catalyst and one with added promoter, supply resin to two nozzles on the spray gun, combining the materials in two V-shaped fan sprays which intersect a short distance outside the nozzles. This system provides a promoted and activated resin. Further blending of these liquids occurs as a result of overlapping passes of the spray on the fiberglass matting.

The resin presently used is a polyester resin, thermosetting, low-pressure, wet-lay-up type, designated as RS 50129. It contains 35% styrene monomer for viscosity control. Shelf life is usually guaranteed for 4 months when the resin is stored at a temperature of 77°F or less; however, the actual life in the field has exceeded two years.

The catalyst used is a benzoyl peroxide emulsion. The benzoyl peroxide content of this material is 40% by weight as a fine particulate matter that remains in suspension for long periods of time. The shelf life of this material has not been fully established, but can be measured in months, not years.

The promoter material is N,N-dimethylaniline. Its function is to initiate decomposition of the benzoyl peroxide catalyst during resin polymerization. It has a freezing point of 36.5°F. Shelf life is unlimited if the material is stored between 36.5F and 90°F; freezing and thawing do not appear to adversely affect the promoter.

The fiberglass material presently in use is a woven roving with random fiberglass backing, supplied as FABMAT C-4020. This is a 40 oz. per square yard woven roving backed by 2 oz. per square foot of random fiber.

Application consumes about one pound of resin and associated components per square foot of fiberglass. Resin gelation time of about 10 minutes is obtained at working temperatures of over 40°F. One or two laminated layers of this FRP have been successfully utilized for expedient soil surfacings under a variety of vehicular loads over a wide range of soil conditions.

As constituted, however, the present system has the following deficiencies:

a. The shelf life of the resin and catalyst components is short when the need for stockpiling these materials as a war reserve stock is considered. It is not clear what factors affect the shelf life of these components, and what techniques could be used to extend the shelf life to a period of five years or more.

b. The system now relies upon close tolerances in metering the flow of promoter and catalyst to provide a rapid (10 minutes) gelation time. Other, less sensitive techniques are needed to assure short gel times.

c. The materials will propagate flames under some conditions. Fire retardancy and/or a self extinguishing capability are necessary features for use of the material in a combat environment.,

d. The FRP can be placed only at ambient temperatures above 40°F. Present Marine Corps requirements show a need for soil surfacings down to temperatures of -65°F and up to 140°F.

The work is specifically addressed to correcting the deficiencies of shelf life by developing techniques and materials to extend the shelf life of chemical components used in FRP soil surfacings to five years or more. However, any formulation developed or spraying unit modification recommended shall not aggravate the other deficiencies listed. While not a contract requirement, it is a further purpose to report promising possibilities for correcting these alternate deficiencies.

SECTION II

SUMMARY

The object of the work is to develop improved chemical components to be used in constructing fiberglass reinforced plastic soil surfacings. The improved components shall (1) have a minimum shelf life of 5 years, and (2) be usable with basic resin spray equipment now used by the Marine Corps.

Accelerated aging studies for shelf stability of resins were conducted at elevated temperature. Resins with improved stability were solicited from resin manufacturers. Inhibitors with proven performance were selected from the literature. The time to gelation versus temperature and inhibitor concentration was measured. A synergistic combination of dinitrophenol and toluhydroquinone was discovered which outperformed other inhibitors. The recommended formulation is 600 ppm of 2:1 2,4-dinitrophenol:toluhydroquinone in SR 3704 resin.

The relative reactivity of resins and catalysts was measured from Sunshine gel time tests, and exothermic reaction - the temperature rise, $\Delta T°C$, and time to peak exotherm. Degree of cure was determined by Barcol hardness. The current AMSS catalyst failed to cure stabilized resin suitably. A new, reliable catalyst system was developed based on cumene hydroperoxide, Vanadium Ten Cem, and N,N-dimethyl-p-toluidine (DMT). The system is adaptable to basic spray equipment. Mixing equipment to prepare Vanadium Ten Cem: DMT promoter solution is necessary. Catalyst and promoter are fluid and pumpable at -25°F. Gel time was easily varied between 10 and 30 minutes over the 40°F to 120°F temperature range by manipulating catalyst concentration. The kinetics of catalysis is fully explained. A gel retarder based on methyl ethyl ketone peroxide to further control gel time was demonstrated.

Mats of fiberglass and resin were prepared by wet lay-up techniques at each temperature of 40°F, 73°F, and 120°F. Flexural and tensile strength was measured by ASTM test methods. At each temperature the mechanical property substantially exceeded contract specifications.

All catalyst components were compared for shelf stability and hazard from a critical examination of literature information and by independent experimental data. The peroxides are chemically unstable and pose a stability and hazards problem. Cumene hydroperoxide is more stable and less hazardous than Cadox 40E. Technically, cumene hydroperoxide can be stored at 60°F for 5 years with less than 10% deterioration; however, peroxide manufacturers recommend against extended storage.

The burn resistance of the developed system is only slightly improved over the AMSS system; both supported combustion on the surface of an FRP mat from burning gasoline.

SECTION III

TESTS

A. SHELF STABILITY TESTS

A three-dram vial filled to the shoulder with resin and capped with an aluminum-lined cap was used for testing. The resin volume and air space in the vial were held constant and approximately 10 grams of resin were used, the exact weight depending on resin density. Care was exercised in testing the gel times because the gel first forms at the bottom of the vessel; thus a completely static test has to be avoided. However, the oxygen in the air space can also reactivate the inhibitor to give falsely long stabilities, and therefore extensive agitation must be avoided.

The vials were carefully inverted to minimize both the mixing of air into the sample and the formation of gel at the bottom of the vial. The samples were checked periodically from hourly at 120°C to biweekly at 50°C. The end point can be anticipated by the decrease rate of bubble rise as viscosity increases. The point at which the air bubble would no longer rise to the top of the vial was taken as the gel point or end of the test.

B. REACTIVITY STUDIES

Reactivity testing consisted of determining the gel time, time to peak exotherm, temperature rise to peak exotherm (ΔT), and degree of cure by hardness (Barcol #934). Determinations were made with a Sunshine gel tester and with a time/temperature recorder.

Samples for the Sunshine gel tests were prepared by thoroughly mixing 10 grams of properly catalyzed resin and pouring the mixture into the Sunshine gel tube to the specified level. The switch controlling the spindle and timer was turned on and the gel time was recorded from the timer on the Sunshine tester.

Samples for the exothermic test were prepared by mixing 20 grams of properly catalyzed resin and pouring the resin into a 2-inch diameter aluminum foil dish. An iron-constantan thermocouple was imbedded in the resin and attached to a temperature recorder. The changes in temperature were used to determine time to peak exotherm and temperature rise (ΔT°C).

C. MECHANICAL TESTING OF GLASS LAMINATES

Laminates were prepared from four plies of 9-inch X 9-inch FABMAT 2418 and properly catalyzed resin at 60:40 resin:glass ratio. The predetermined resin, catalyst, promoter, and glass were weighed on a Mettler balance. The first ply of glass was placed on a Mylar sheet. The resin, catalyst, and promoter were mixed thoroughly and enough resin to completely wet the glass was placed on the first ply and rolled with a grooved metal roller until the resin completely wet the glass. The remaining glass and resin were alternately added and rolled until the laminate was completed. The laminate was cured at room temperature (75°F), then cut into 1-inch wide specimens. The edges of the specimens were milled smooth and parallel on a Tensilcut milling machine using a diamond burr cutter. The specimens were tested on an Instron tensile tester for flexural and tensile properties as specified in the ASTM procedures. With FABMAT C-4020, two plies of glass mat were used. Temperature of application was varied by preconditioning components in a Conrad Environmental Chamber and applying to the fiberglass analogously at the temperatures specified.

D. FLAME PROPAGATION TESTS

The test for flame propagation consisted of a 9-inch X 9-inch laminate, held at an incline of 45°, with a reservoir of burning gasoline (5cc) attached to the lower edge. The flame, if it ignited the surface, either propagated or gradually extinguished itself after the gasoline burned out. The total time of combustion was recorded as a measure of the tendency of the composition towards flammability.

Specimens were cured at room temperature. The AMSS resin was cured with 2.5 phr Cadox 40E and 0.5 phr dimethylaniline. Stabilized resin was cured with 1.0 phr cumene hydroperoxide and 0.25 phr promoter.

SECTION IV

IMPROVED CHEMICAL COMPONENTS DEVELOPMENTS

A. STABILIZATION OF RESINS

Initially, shelf stability studies were made on aged resins: RS 50129 obtained from Port Hueneme and designated RS 50129 (PH) and the Kirtland AFB Primary resin (on hand).

The studies were expanded as new inhibitors, selected[1] for their effectiveness in increasing the shelf life of polyester resins, and new resins were received. The new resins from PPG were variations of RS 50129 with added stabilizer to increase shelf life. Alpha Chemical Corp. also supplied resins.

1. Inhibitor Studies

The concentration of the inhibitor in the resin and the temperature of storage were varied. The time lapse to gelation is the shelf life of the resin system at the respective temperature selected (Table XII—Appendix). Inhibitors which gave the longest shelf life were selected for further study. The 2,4-dinitrophenols as a class gave the best stability. However, in plotting shelf life versus stabilizer concentration, an important discovery was made that dinitrophenols and toluhydroquinone were synergistic in their stabilizing effect (Table XII, samples 12-16, 19-22, 23-26); and illustrated in Table I.

TABLE I

SYNERGISTIC STABILIZATION

Stabilizer, 600 ppm[a]	Shelf Life at 120°C	Shelf Life at 80°C
Toluhydroquinone (THQ)	5.0 hrs.	112 hrs.
Dinitro-ortho-secondary-butylphenol (DN)	7.3 "	176 "
2:1 DN:THQ[b]	9.3 "	264 "

a. ppm, parts of inhibitor per million parts of SR-3703 resin (0.06%)
b. 400 ppm DN, 200 ppm THQ

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[1] Wright-Patterson AFB, "Investigation of Materials and Methods of Extending the Shelf Life of Polyesters," by Eldon E. Stahly, E. W. Lard, D. A. Daniels, and M. Rock, AFAPL-TR-68-49, (July 1968, W. R. Grace & Company).

Thus, 600 ppm of a 2:1 blend of DN in THQ gave better stability than either stabilizer alone. The 2:1 blend by weight appears to be a 1:1 mole ratio of DN:THQ. The best, and recommended system, is 400 ppm 2,4-dinitrophenol:200 ppm toluhydroquinone in SR 3704[2] (600 ppm 2:1 DNP:THQ, #82, Table XII). The stability at 120°C was 11.5 hours, and 312 hours at 80°C.

A shelf life of 5 years at 75°F for any given resin system can be predicted from the elevated temperature studies. A family of parallel straight lines is obtained when shelf life is plotted[3,4] against temperature for the various formulations. Selected data from Table XII are plotted in Figure 1 as representative of typical graphics. The stabilized resin, whose line intercepts the point at 5 years and 75°F, would fulfill the requirements of the contract. RS 50129 (as SR 3703) and SR 3704 would not have adequate stability. The predicted shelf life of SR 3703 (RS 50129) is about one year. Field experience on stored RS 50129 has indicated a longer period. Predicted shelf stability from accelerated aging studies may therefore be conservative; however, they are accurate in principle.

Temperature has a significant effect on shelf life, because of the sharp slope of the curve. A resin stable for 5 years at 75°F would be stable for only 4 years at 78°F. The 3°F spread over 5 years would shorten the shelf life by 1 year; conversely, a 10 year shelf life appears feasible if the resin is stored at 65°F. Storage of resin under conditions which neutralize temperature fluctuation is recommended, such as in white drums, in sheds or shaded areas, or even underground. Drums should be horizontal with the bungs covered with resin because vapor phase polymerization appears to initiate at a bung opening.

2. Viscosity Drift with Accelerated Aging

The line which intercepts 5 years/75°F and 3.5 hours/120°C conforms to traditional shelf life studies where gelation occurs. Viscosity increases of samples in the oven were observed, and resin systems which had longer shelf lives were more fluid at 3.5 hours. Stability studies were therefore shifted and expanded to determine viscosity drift during accelerated storage.

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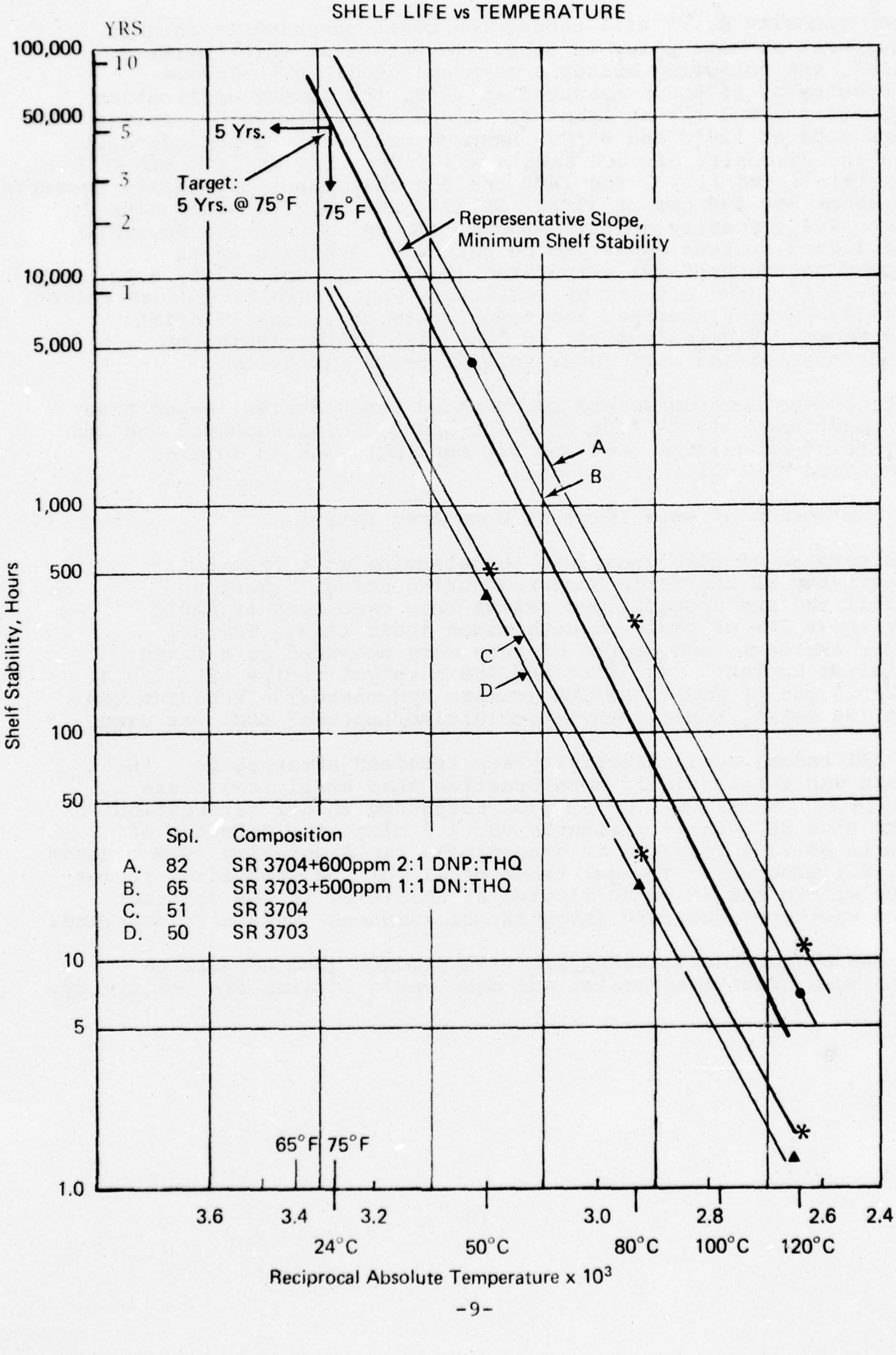
[2] SR 3704 is RS 50129 modified with slighty more of the same inhibitor used in RS 50129.

[3] Kirtland AFB, "Expedient Surfacing Materials", by H. E. Filter and S. S. Drake, AFWL-TR-73-70, (October 1973, The Dow Chemical Co.).

[4] E. W. Lard, R. G. Rice, E. E. Stahly, "Storage Stability of Unsaturated Polyesters", Ind. Eng. Chem. Prod. Res. Develop., Vol. 10, No. 4, P. 391 (1971).

Figure 1

SHELF LIFE vs TEMPERATURE



The viscosity drift will render the resin unsprayable in AMSS equipment at some point in time. To establish this "working life", the following criteria were proposed: (1) maximum viscosity of 1600 cps measured at 40°F, the lowest application temperature, and (2) at least 3.5 hours aging at 120°C. Resins were aged at 120°C and 80°C. Samples were removed periodically, and the viscosity of each sample was determined at 75°F and 40°F (Tables II and III). The 1600 cps for suitable sprayability converts to about 300-350 cps at 75°F. SR 3703 and SR 3704 would have excessive viscosity drift. (Table II, spl. 2 and 6.) Several stabilized systems appear to be suitable, approaching or exceeding the criteria stipulated (Table II, spl. 4, 5, 8-12; and Table III). The effects of inhibitor type, inhibitor concentration, initial resin viscosity, and temperature on viscosity drift are shown. Viscosity drift is less with higher inhibitor concentration and with lower initial resin viscosity.

The optimum compromise and recommended resin system, based also on reactivity, is SR 3704 plus 400 ppm 2,4-dinitrophenol and 200 ppm toluhydroquinone (600 ppm 2:1 DNP:THQ) with an initial specified viscosity of 190 cps.

3. Retention of Reactivity of Oven Aged Resins

The purpose of this study was to determine if a change in reactivity of the resin occurred during aging. Various stabilized and unstabilized resins were oven aged at 120°C for about 70% of their predetermined shelf life. The gel time, exotherm, and degree of cure were measured at a fixed catalyst content. The Kirtland AFB catalyst recipe of 1.0/0.4/0.2/0.3 phr of CHP/V/DMT/DDM (cumene hydroperoxide/Vanadium Ten Cem (5% metal)/N,N-dimethyl-p-toluidine/Lupersol DDM) was used.

In all cases, resin reactivity was retained after aging. "Neat" resin was substantially more reactive than stabilized resin (Table IV, 4-10, 16-21). SR 3704 responded to gel retardation more than SR 3703 (9.1 minutes vs. 2.9 minutes); deletion of DDM in SR 3704 resulted in exceedingly rapid gelation (0.9 minutes vs. 9.1 minutes). The gel times of all of the stabilized resins were within the 10 to 30 minutes as specified in the contract. Good exotherms and cure (high Barcol hardness) were also obtained.

Cumene hydroperoxide catalysis will produce good properties with aged stabilized resin, and aged resin retains its reactivity.

TABLE II

VISCOSITY DRIFT WITH ACCELERATED AGING

Sample	Resin System	Stabilizer	Time at 120°C hrs:min	Viscosity at 75°F cps
1	RS 50129(PH)	As Received	None	295
			1:00	290
			2:00	472
2	SR 3703	" "	None	142
			0:30	155
			1:00	178
			1:15	298
3	"	300 ppm 2:1 DNP:THQ	5:30	920
4	"	450 ppm 2:1 DNP:THQ	5:30	470
5	"	600 ppm 2:1 DNP:THQ	5:30	390
				1780 at 40°F
6	SR 3704	As Received	None	142
			0:30	155
			1:00	155
			1:30	290
7	"	300 ppm 2:1 DNP:THQ	5:30	740
8	"	450 ppm 2:1 DNP:THQ	5:30	360
9	"	600 ppm 2:1 DNP:THQ	5:30	285
10	SR 3704[a]	600 ppm 2:1 DNP:THQ	5:30	340
				2000 at 40°F
11	SR 3704[b]	600 ppm 2:1 DNP:THQ	5:30	340
				1610 at 40°F
12	SR 3705	1000 ppm THQ	None	142
			1:10	155
			2:20	170
			3:30	236
			4:40	392

[a] Sample from metal container transferred to a bottle and stored on bench top

[b] Sample directly from container

TABLE III

VISCOSITY DRIFT WITH ACCELERATED AGING

Resin Systems

Time at 120°C hrs:min	SR 3704[a] plus 600 ppm 2:1 DNP:THQ Viscosity, cps 75°F	40°F	SR 3704[a] plus 1000 ppm 2:1 DNP:THQ Viscosity, cps 75°F	40°F
None	180	770	170	780
1:00	200	860	193	800
2:00	240	910	225	900
3:00	272	1200	260	1140
4:00	340	1560	288	1390
5:10	505	2300	365	1790
6:00	710	3450	480	2190
7:00	1180	5100	640	3100
8:00	3700	13000	900	4200

SR 3705 plus 600 ppm 2:1 DNP:THQ

Time at 120°C hrs:min	Viscosity, cps 75°F	40°F
None	142	650
1:00	155	670
2:00	180	740
3:00	193	935
4:00	245	1160
5:42	330	1570
6:00	406	1930
7:00	580	2660
8:00	820	3850
9:00	(1300)	----
10:00	(3100)	----
11:00	(10,000)	----

Time at 80°C hrs.	Viscosity, cps 75°F	40°F
None	155	690
51	272	1010
100	295	1370
150	417	2100
200	625	3000
250	1070	5200

[a]SR 3704, from RS 50129 production (Oct. 1976)

TABLE IV

RETENTION OF REACTIVITY OF OVEN AGED RESINS

Sample	Resin System	Stabilizer	Time at 120°C hrs:min	Reactivity[a] Gel Time,	$\Delta T°C/min.$	Hardness Barcol #934
1	RS 50129(PH)	600 ppm 3:1 DNP:THQ	5:30	15.4 min.	122/26	42-44/38-42 [b]
2	"	" 3:1 DN:THQ	"	17.3	121/17	38-46/34-37
3	"	" 3:1 PA:THQ	"	14.6	116/22	41-46/28-33
4	SR 3703	As Received	None	2.9	168/5	Hard/Crazed
5	"	"	0:51	2.4	159/4	"
6	SR 3704	"	None	0.9[c]	Too fast	"
7	"	"	1:00	0.5[c]	" "	"
8	"	"	None	9.1	156/11	"
9	"	"	1:14	10.5	155/18	"
10	"	"	1:00	9.9	---	---
11	"	600 ppm 2:1 DNP:THQ	None	18.6	147/21	40-45/34-41
12	"	"	5:30	23.3[d]	134/28	44-45/34-40
13	"	"	"	18.7	137/24	45-48/42-46
14		"	None	18.9	145/21	45-47/40-41
15	"	"	5:30	19.6	135/24	47-50/35-41
16	SR 3705	As Received	None	5.3	150/8	Hard/Crazed
17	"	"	1:24	5.1	153/7	"
18	SR 3706	"	None	1.9	149/4	"
19	"	"	2:06	1.9	161/4	"
20	SR 3707	"	None	3.1	169/5	"
21	"	"	2:06	1.8	158/6	"

[a]Catalyst: CHP/V(5%)/DMT/DDM = 1/0.4/0.2/0.3 phr

[b]Top/Bottom of a 20 g. disc, 2" diameter X 1/4" thick

[c]DDM deleted from catalyst

[d]Time lapse 30 minutes after promoter added before adding CHP vs. Spl. 13

B. STABILITY OF CATALYST COMPONENTS

Each of the potential catalyst components was examined in regard to stability for 5 years. Preliminary data from the literature[5] on shelf stability of peroxidic components indicate cumene hydroperoxide to be the most thermally stable and should have the longest shelf life; Cadox 40E is the least stable.

The relative ten hour half life values reported are:

Cadox 40 E	71°C
Lupersol DDM	105°C
Cumene Hydroperoxide	158°C

Extrapolated calculations gave values of over 100 years for 50% decomposition of CHP, 5 years for DDM, and 1 year for Cadox 40E. The half life tests are run on benzene solutions, not on "neat" compounds, therefore the values reflect relative stability.

Experimental data from hazards simulation studies on Cadox 40E and calculations on CHP & DDM support the relative stability of CHP, DDM, and Cadox 40E (Figure 2). Maximum safe storage temperature depends upon the container, which has a characteristic heat transfer coefficient. Relative data are tabulated for a 55 gal. drum (Table V).

TABLE V

MAXIMUM SAFE MATERIAL[a] TEMPERATURE

Peroxide	Temperature
Cumene Hydroperoxide	90°C (194°F)
Lupersol DDM and MEKP	68°C (154°F)
Cadox 40E	53°C (127°F)

[a]Assumed 6 hours heat build up based on heat exchange calculation. Temperature is measured internally at center of container (i.e., maximum value). Safety factor of 10°C recommended for storage.

The storage temperature for less than 10% deterioration in 5 years was calculated from hazards simulation and half life data (Table VI).

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[5]Lucidol Division, Pennwalt, Corp., Bulletin 30-30; Noury Peroxide Bulletin

Figure 2
THERMAL RUN AWAY CURVES

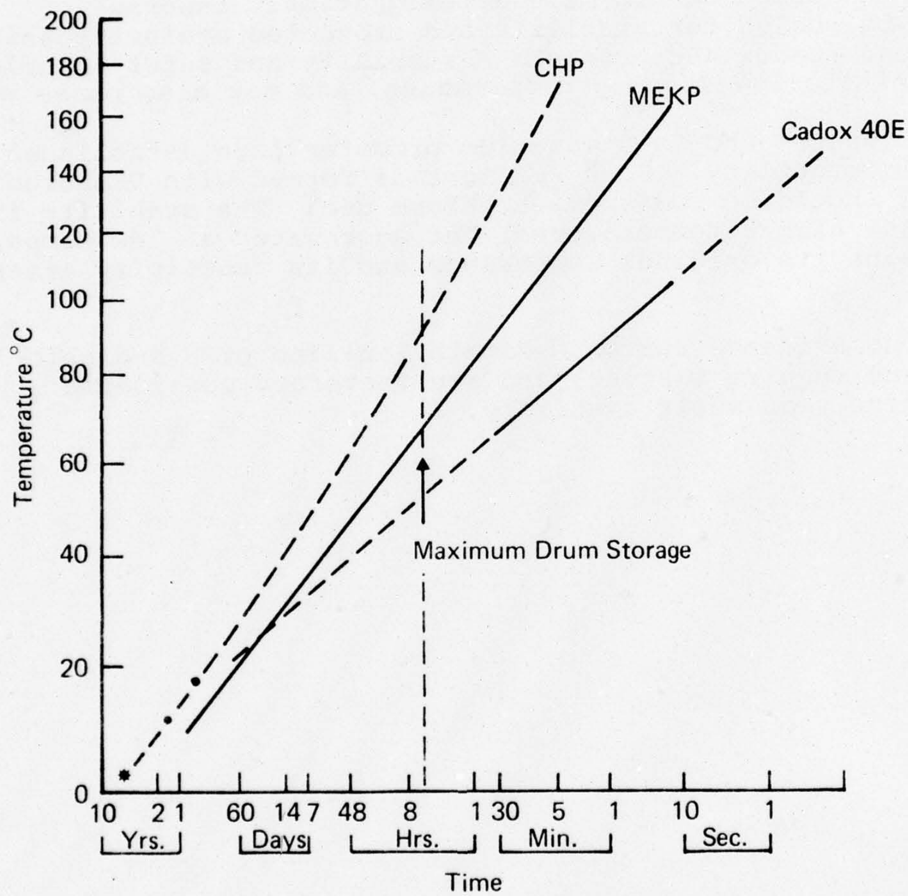


TABLE VI

STORAGE TEMPERATURE

Peroxide	Temperature, °F
Cumene Hydroperoxide	63
Lupersol DDM	58

Cumene hydroperoxide is safe to store at ambient conditions, but must be cooled to minimize deterioration. Lupersol DDM must be cooled for stability and protected against possible detonation. Cadox 40E presents a stability and safety problem, because of its low storage temperature, and may also phase separate.

Vanadium Ten Cem and VN-2 vanadium promoter have established 5 year shelf stability. Some sediment is formed with Vanadium Ten Cem which should be redispersed before use. The stability is improved at higher temperatures, but aggravated at low temperature. VN-2 retains its original appearance and its reactivity after 5 years.

There is no evidence that N,N-dimethylaniline or N,N-dimethyl-p-toluidine require testing, and are therefore considered to have five year shelf stability.

SECTION V

REACTIVITY STUDIES

Many of the resin systems tested for shelf stability were also tested for response to catalysis. Thus, the variables measured are resin, inhibitor type, inhibitor combinations, inhibitor concentration versus catalyst-type and concentration of components, and temperature. The catalysts tested were BPO/DMA (components used in AMSS presently), a standard cobalt naphthenate/methyl ethyl ketone peroxide (MEKP as Lupersol DDM), and CHP/V. An alternate source of vanadium promoter was obtained and evaluated.

A. CATALYSIS

The gel time, as a direct measure of reactivity, was obtained on 10 grams of a properly catalyzed resin mixture in a Sunshine Gel Time Meter; concurrently, the time/temperature exothermic reaction was recorded on a Brown Electronik Recorder for 20 grams (2" diameter, 1/4" thick) of the catalyzed mixture. Barcol hardness was used as a measure of cure. The complete study is reported in Table XIII (appendix).

The catalyst optimization studies and the failure of the Cadox 40E to cure stabilized resin are particularly significant. The experimental design variation of catalyst components to optimize composition are reported in Table VII. When CHP and Vanadium Ten Cem (V) are used as the sole catalyst components, reactivity is low but good cures are attainable. An optimum ratio of CHP/V exists: too little or too much V Ten Cem results in poor cure (low Barcol hardness #2 and #5). The optimum CHP: V Ten Cem ratio is 6.7:1, but the range of 10:1 and 6:1 (#3 and #4) all have good Barcol values thereby tolerating a latitude in composition preparation. Dimethyltoluidine (DMT) has a marked effect on accelerating gelation to give very fast gel times (#6 or 7 vs. #4).

Gel times can also be changed by manipulating total catalyst concentration (#8 or #9), and further controlled by using Lupersol DDM gel retarder (#10 and #11). The study has shown that DMT is necessary for fast cure, but the quantity can be reduced from the Kirtland AFB promoter recipe of 2:1 DMT:Vanadium Ten Cem (by volume) to 0.66:1. Because DMT is corrosive and may be toxic (like DMA), the reduction is favorable both logistically and safety-wise.

Cure at 120°F was successfully demonstrated with good hardness and control of gel time at very low catalyst concentrations (#12 to #17). Cure at 40°F is also shown (#18 to #24). The Barcol hardness values are particularly high showing that excellent cure has been obtained, even at 40°F.

TABLE VII

CATALYST OPTIMIZATION WITH STABILIZED[a] SR 3704

Sample	Catalyst Component, phr CHP	V	DMT	DDM	Gel Time, min.	Barcol Hardness Top/Bottom
			Room Temperature Cure, 74°F			
1	0.5	0.1			72	31-40/27-34
2	2.0	0.1			67	8-14/8-16
3	2.0	0.2			30	43-46/40-44
4	2.0	0.3			25	48-49/42-46
5	2.0	0.6			28	1/1
6	2.0	0.3	0.1		4.3	46-49/44
7	2.0	0.3	0.2		3.0	45-48/40
8	1.0	0.15	0.1		13.1	45-48/47-50
9	1.0	0.15	0.2		11.1	45-38/45-47
10	1.0	0.15	0.2	0.1	22.0	44-45/43-44
11	1.0	0.15	0.2	0.2	40.8	41-44/41-45
			High Temperature Cure, 120°F			
12	0.5	0.075	0.05		10.9	44-47/41-45
13	0.5	0.075	0.05	0.1	12.5	42-43/41
14	0.5	0.075	0.05	0.2	22.8	44-46/40-41
15[b]	0.5	0.075	0.05		11.9	OK
16[b]	0.5	0.075	0.05	0.25	23.4	OK
17[b]	0.5	0.075	0.05	0.30	30.6	OK
			Low Temperature Cure, 40°F			
18	2.0	0.3[c]	0.2[c]		9.0	43-47/41-44
19	2.0	0.3[c]	0.2[c]	0.1	47.7	44-48/46-47
20	2.0	0.3[c]	0.2[c]	0.2	102.0	49/46-47
21	1.5	0.225[c]	0.15[c]		15.7	47-50/47-49
22[b]	2.0	0.3	0.2		22.1	40-44
23[b]	2.5	0.375	0.25		12.7	36-40
24[b]	2.0	0.3[c]	0.2[c]		14.4	42-46

[a]Stabilized with 600 ppm 2:1 DNP:THQ

[b]Different Lot of SR 3704 from production material (Marine Corps., Oct. 1976)

[c]Vanadium Ten Cem combined and added as a single component.

The failure of the present AMSS catalyst system to cure stabilized resin is reported in Table VIII.

TABLE VIII

CADOX 40 E CATALYSIS

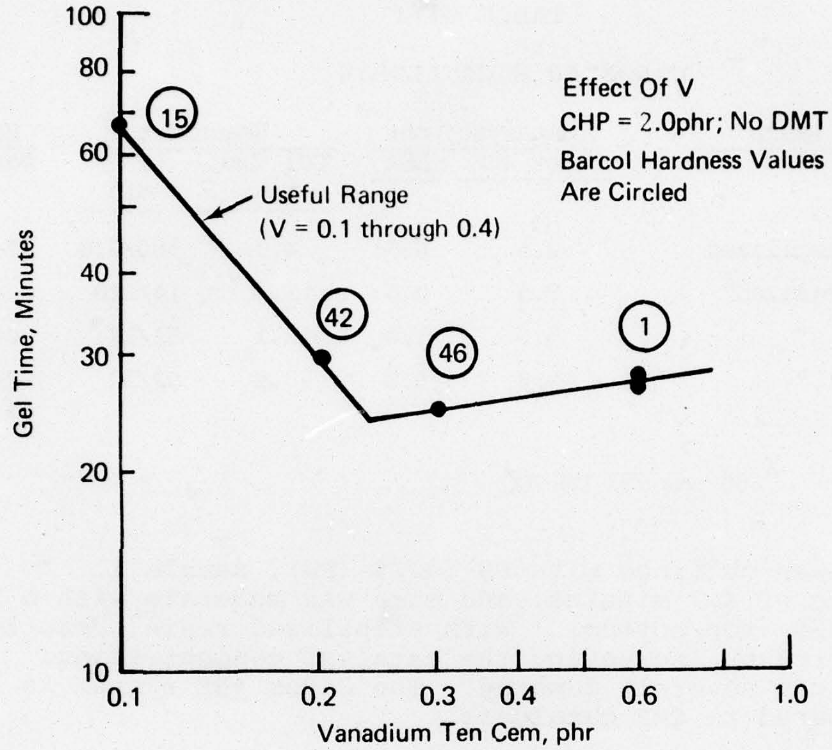
Sample	Resin	Catalyst, phr		Reactivity		Hardness
	RS 50129 (PH)	Cadox 40E	DMA	Gel Time, min.	ΔT°C/min	Barcol #934
1	Unstabilized	2.5	0.5	4.7	100/8.8	27-29/8-10
2	Stabilized[a]	2.5	0.5	45.0	14/220	0/0
3	"	5.0	1.0	10.1	>51/17	0-1/0-1
4	"	5.0	0.5	17.8	92/32	7-12/2-7

[a]600 ppm 2:1 DN:THQ

Good response was obtained with RS 50129 (PH), sample 1, with a gel time of 4.7 minutes, and cure was moderate with a Barcol hardness of 28/9 (top/bottom). With stabilized resin, reactivity could be restored by increasing the catalyst concentration; however, cure was severely damaged. The Cadox 40E system is very slow compared to CHP catalysis.

The fundamental kinetics of CHP/V/DMT catalysis are shown in Figures 3 to 6 (as plots from Table VII data). As noted from the slopes of the curves, CHP has very little effect on gel time (Figure 3). CHP is the principle peroxy compound necessary for cure, however. Vanadium has the greatest effect on gel time (Figure 3). An unusual change in the rate of gelation occurred at 0.6 phr Vanadium Ten Cem verified by repetition, with a corresponding loss of cure as indicated by the low Barcol Hardness. Too much vanadium is detrimental to good cure, hence the ratio of 2.0:0.6 CHP:V Ten Cem (10:3) or lower ratios are to be avoided. Dimethyltoluidine had a minor effect on rate, but a significant effect on cure. The slopes (Figure 4) at both 1.0 and 2.0 phr CHP are shown to be essentially the same. The effect of DMT is independent of CHP. V and DMT in combination is the most important component to control gel time. The solution of 3:2 V:DMT (by volume) is designated Promoter PH. The effect of DDM (Figure 4) is shown twice: when plotted (1) independently, and (2) relative to DMT. The change in slope from negative to positive means that DDM is retarding gelation. The potential use of DDM is more thoroughly discussed on page 26.

Figure 3
CATALYST COMPONENT STUDY
(Stabilized SR 3704, 600 ppm 2:1 DNP:THQ)



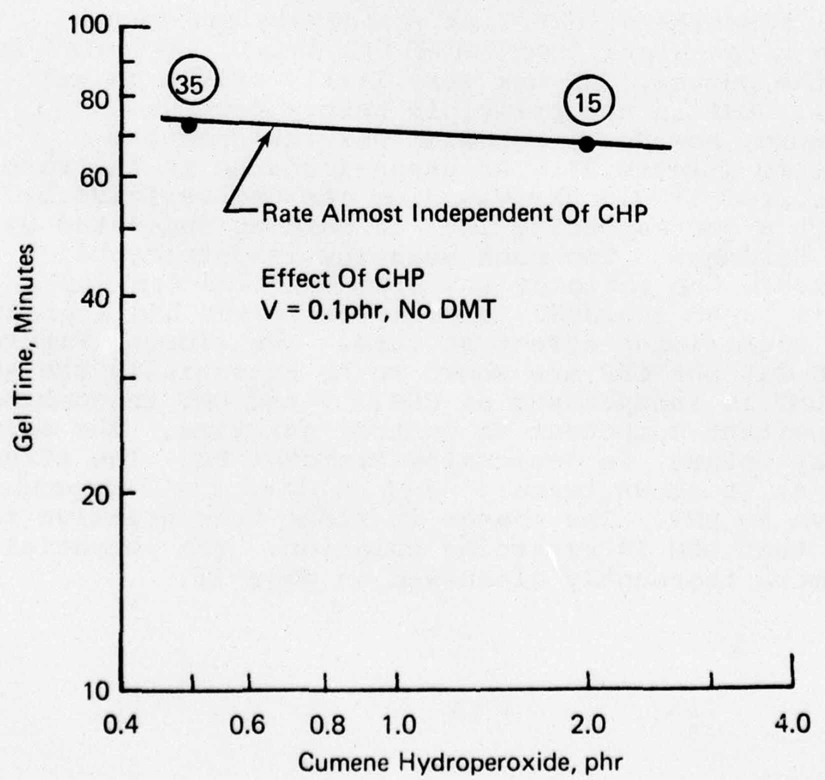


Figure 4
CATALYST COMPONENT STUDY
(Stabilized SR 3704, 600 ppm 2:1 DNP:THQ)

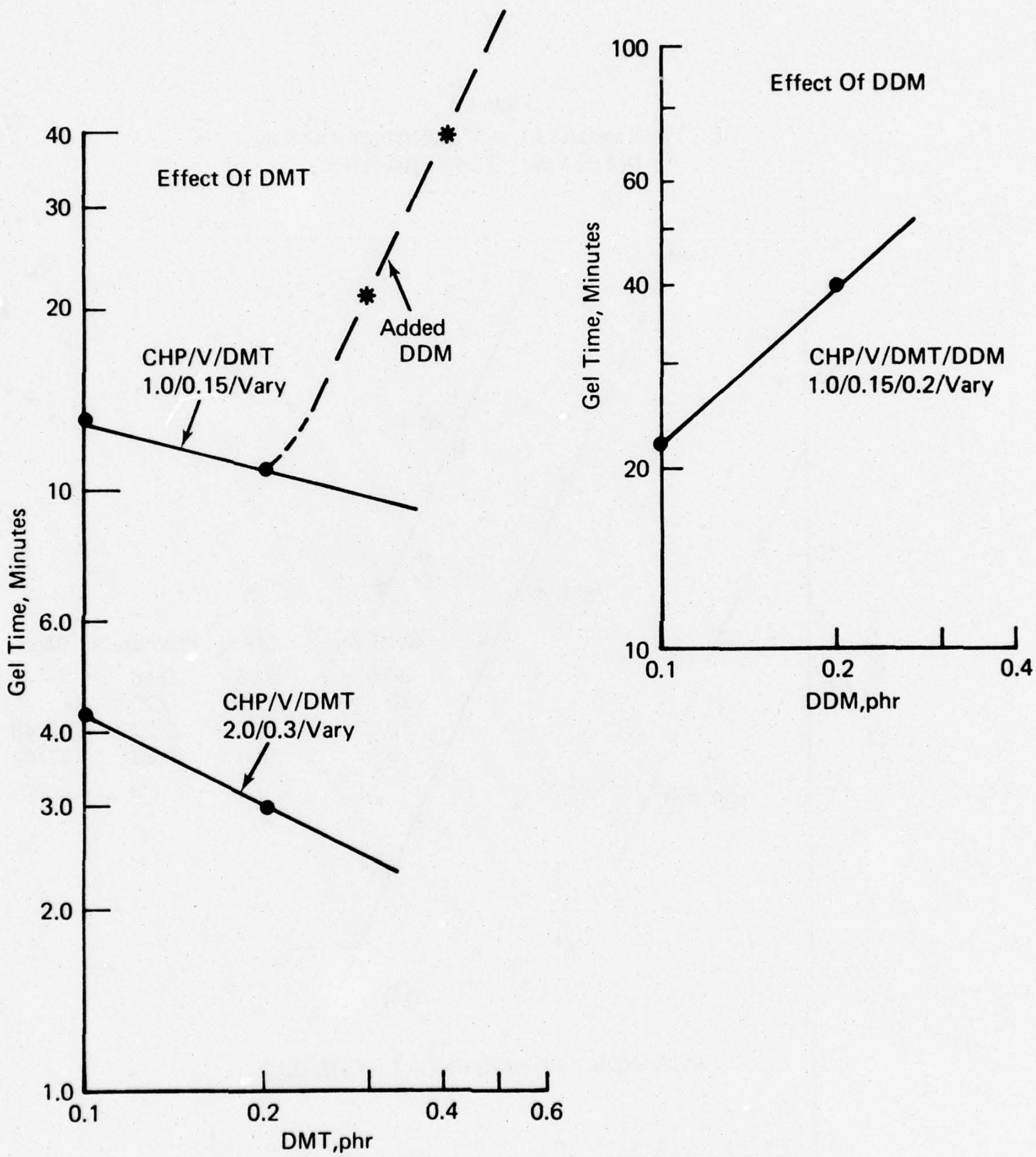


Figure 5

GEL TIME vs CATALYST CONCENTRATION
AT DIFFERENT TEMPERATURES

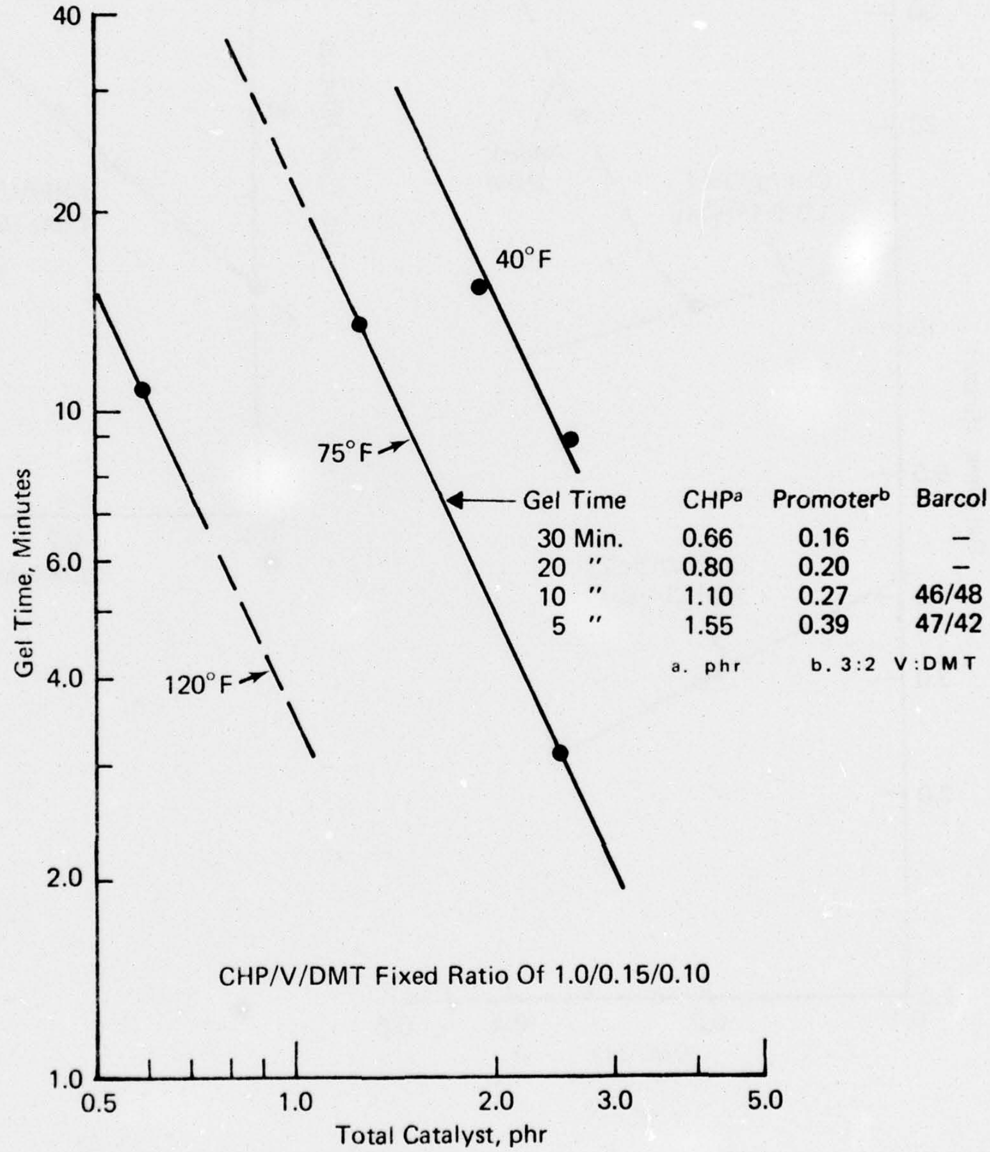
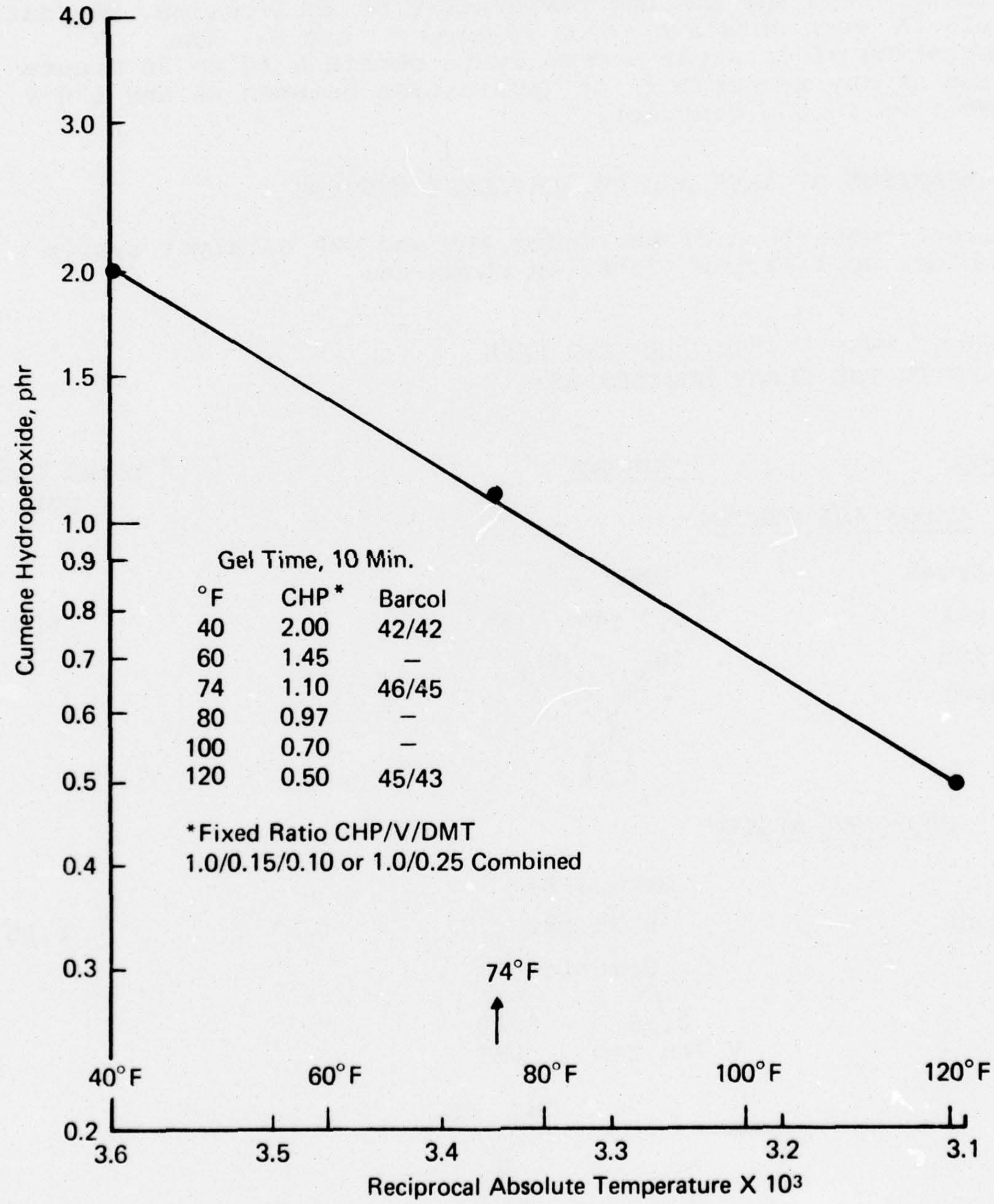


Figure 6
SELECTION OF CATALYST CONCENTRATION
vs TEMPERATURE OF APPLICATION
(Constant Gel Time, 10 Minutes)



The change in gel time with temperature of application, or the correction in catalyst concentration to maintain proper reactivity for both low and high temperatures, are depicted in Figures 5 and 6. Thus, a constant gel time of 10 minutes is obtained at 40°F, 75°F, and 120°F using 2.5, 1.37, and 0.625 phr total catalyst respectively. The CHP concentration versus temperature is shown in Figure 6. The promoter is automatically 25% of the CHP because a fixed ratio of CHP to promoter is used (1.0/0.25). The CHP concentration is selected from the ambient temperature of application. The data in Table IX were obtained from Figures 5 and 6: the concentration of catalyst necessary to obtain a 10 to 30 minute gel time at any temperature of application between 40 and 120°F as specified in the contract.

B. COMPARISON OF AMSS AND CHP CATALYST SYSTEMS

The direct comparison of the Cadox 40E and CHP catalyst system for ambient application (75°F) is shown as:

PRESENT AMSS SYSTEM USES TWO FEED
LINES TO THE SPRAY NOZZLES AS:

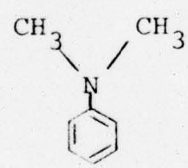
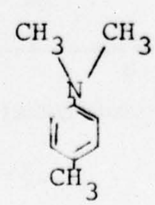
Catalyst	Promoter	Total Catalyst, phr
CADOX 40E SYSTEM		
S0046 Green	DMA	
2.5 phr	0.5 phr	3.0
Cadox 40E (40% BPO)		
PROPOSED SYSTEM		
CHP	Prom. (PH)	
1.0 phr	0.25 phr Solution	1.25
	0.15 V Ten Cem / 0.10 DMT	
		

TABLE IX

CATALYST CONCENTRATION VERSUS TEMPERATURE

Temperature °F	Catalyst[a], phr for a gel time of: 10 minutes CHP	10 minutes Prom. (PH)[b]	30 minutes CHP	30 minutes Prom. (PH)[b]
40	2.00	0.500	1.20	0.30
45	1.86	0.465	1.10	0.27
50	1.66	0.415	1.01	0.25
55	1.53	0.383	0.93	0.23
60	1.40	0.350	0.87	0.22
65	1.25	0.313	0.78	0.20
70	1.15	0.288	0.72	0.18
75	1.11	0.278	0.66	0.17
80	0.98	0.245	0.61	0.15
85	0.87	0.218	0.56	0.14
90	0.80	0.200	0.52	0.13
95	0.74	0.185	0.47	0.12
100	0.68	0.171	0.44	0.11
105	0.64	0.160	0.40	0.10
110	0.59	0.148	0.36	0.091
115	0.55	0.137	0.34	0.084
120	0.50	0.125	0.31	0.077

[a]phr, parts per hundred parts of resin, stabilized SR 3704

[b]Promoter (Port Huememe) 3:2 Vanadium Ten Cen (5% metal): N,N-Dimethyl-p-toluidine (by volume)

Conclusion of CHP Catalysis

1. Less total catalyst
2. Greater reactivity and reliability
3. Corrosive component, DMT, at only 20% DMA and further diluted to only 40% solution in V Ten Cem.
4. Pumpable at -25°F.

A mixing step to prepare Promoter PH solution must be added to the present AMSS operation.

C. GEL RETARDATION

The use of Lupersol DDM to retard gelation is selectively shown at each of the temperatures (Table VII). The control of gel time with DDM offers the opportunity to develop a less sensitive catalyst system and still get good cure. Sample 20 gelled after one hour and 42 minutes at 40°F, but cured with high Barcol hardness.

In another of many examples (Table XIII, spl. 37-39) Lupersol DDM was tested as a gel retarder with RS 50129 with excellent response. The gel time was extended from 3 minutes to 65 minutes with as little as 0.2% gel retarder. The cured resins had good hardnesses; intermediate gel times are easily obtained with proper amounts of gel retarder between 0.05 and 0.2%.

To be useful in AMSS equipment, without modification, however, requires that the peroxide be added as a single component. A 23% solution of DDM in CHP (0.3 part of DDM in 1.0 part of CHP) was used as the single catalyst component and compared to the corresponding reactivity obtained by separate addition of CHP and DDM. The comparison is shown in Table X.

TABLE X

RELATIVE REACTIVITY OF COMBINED CATALYST/GEL RETARDER[a] ON STABILIZED SR 3704

Sample	Inhibitor 600 ppm	Separate Addition Gel Time, min.	Separate Addition Barcol Top/Bottom	Combined Gel Time, min.	Combined Barcol Top/Bottom
1	Control (no DDM)	2.5	37-40/30-33	---	----
2	DNP	30.8	41-45/31-40	27.1	40-43/36-42
3	DN	26.5	35-45/30-35	61.0[b]	37-41/31-39
4	PA	9.1	41-45/25-30	8.0	40-43/22-24
5	THQ	12.1	36-40/26-33	16.5	44-45/33-36

[a]Catalyst concentration CHP/Prom. K/DDM 1.0/0.6/0.3 phr

[b]Catalyst components at 1/2 concentration level.

The excellent agreement between separate and combined addition of catalyst/gel retarder to control gel time indicates that the proposed CHP/V system can be adapted to present AMSS equipment. Only two feed lines of catalyst (DDM solution in CHP) and promoter would be used. Further control of gel time from 26 to 61 minutes by adjusting catalyst concentration is shown by sample 3.

Vanadium Ten Cem was withdrawn from the market; however, discussions with personnel at Mooney Chemical Company indicate that they will make it on a customer demand basis. An investigation of alternative vanadium promoters was undertaken as an added precaution. Samples of Noury's VN-2 and VN-3, acquired about four years ago, were tested for comparative reactivity. Some 60 gel tests were run (Table XIII), mostly on new stabilized SR 3704, comparing VN-2 to Vanadium Ten Cem, varying temperature and stabilizer, and preparing fiberglass reinforced mats. VN-2 is a viable replacement for Vanadium Ten Cem although higher concentrations of VN-2 are needed relative to Vanadium Ten Cem for equivalent reactivity.

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SECTION VI

PHYSICAL AND MECHANICAL PROPERTIES

Fiberglass reinforced composites of SR 3705[6] and production SR 3704[6] were made with Fabmat 2418 and 4020, in the required recipe of 60/40 resin/fiberglass. Tests were run at 40°F, 74°F, and 120°F, using catalyst concentrations specified in Table IX and other combinations as shown in Table XI. Reactivity of excess resin from the mat preparation and in the corresponding mat was measured. Reactivity, Barcol hardness, flexural strength , and tensile strength are shown in Table XI.

Gel time of excess resin corroborated reactivity of the formulation; gel times in the mat were slower by about 50%. High Barcol hardnesses were obtained. Specifically shown is the resin of choice, SR 3704 with 600 ppm 2:1 DNP:THQ cured at 40°F, 73°F, and 120°F. The strength properties of the contract were exceeded at all temperatures. For sample 12, using Fabmat C-4020, the flexural strength was 40,800 psi (required 28,800 psi), and tensile strength was 20,500 psi (required 13,000 psi). Further mechanical tests were deemed unnecessary because the base AMSS resin was used and good cure was obtained.

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[6]Stabilized, 600 ppm 2:1 DNP:THQ

Table XI

MAT[a] STUDIES

Sample	Resin System	Appl. Temp. °F	Catalyst, phr CHP	Catalyst, phr Prom. PH	Catalyst, phr DDM	Reactivity Gel Time, min. Excess Resin	Reactivity Gel Time, min. In Mat	Peak Exotherm Excess Resin	Peak Exotherm In Mat	Hardness Barcol #934 Top/Bottom	Flexural Strength psi[d]
1	SR 3705	74	0.75	0.19	---	8.5	25	15	45		
2	+ 600 ppm	"	1.00	0.25	0.1	10.5	17	16	27	57/46	
3	2:1 DNP:THQ	"	"	"	0.2	26.0	32	33	--	54/58	
4	"	40	2.0	0.5	---	10.0	14	14	17	---	
5	SR 3704	73	0.75	0.19	---	14	25	18	80	53/62	45,200[b]
6	+ 600 ppm	"	1.0	6.25	---	8	17	12	26	54/64	37,800[b]
7	2:1 DNP:THQ	"	"	0.3%VN2/0.2%DMT		15	25	19	53°C/78min.	55/58	42,300
8	"	"	1.5	0.45%VN2/0.3%DMT		8	10	11	142°C/14min.	55/55	33,000
9	"	40	2.0	0.3V/0.2%DMT		---	25	--	109°C/39min.	56/60	35,400
10	"	120	0.5	0.075%V/0.05%DMT		5	9	--	129°C/22min.	58/60	42,800
11	"	"	"	0.075%V/0.05%DMT/ 0.5%DDM		23	27	--	124°C/----	63/65	46,500
12	"	73	1.0	0.25		---	15	--	85°C/26min.	56/60	40,800[b,c]

[a]Formulated with 4 ply Fabmat 2418 except 12 which had 2 ply Fabmat 4020 (from Port. Huem.)

[b]Fiberglass content analytically from pyrolysis: (5) 44% (6) 43.6%, (12) 41.3%

[c]Tensile Strength: 20,500 psi; ASTM D638-68

[d]ASTM D790-66

SECTION VII

"STAND-BY" PLANT ECONOMICS

The calculation of the economics for a 1-5 million pound/year "stand-by" resin plant were discussed with Dow economic evaluation specialists. The cost of a "stand-by" resin plant which would be started up and operated only when the material is needed is very costly compared to having the resin readily available from a producer. A much better and less costly approach would be to make a contract with a resin manufacturer to "maintain a living specification" on the resin of choice. Such a contract would embody an annual fee to maintain the "living specification" for a designated (5 years or more) period and a commitment to supply the resin within 3-6 months of notice. The time to obtain the resin would be much less than the time required to start up and operate a "stand-by" plant.

Several of the major polyester manufacturers ought to be interested in such a contract since one million pounds of resin represent about 0.1% of the total industry production of one billion pounds/year. The following manufacturers: Reichhold Chemical Industries, W. R. Grace Co., Alpha Chemical Co., Ashland Chemical Co., Freeman Chemical Co., Pittsburgh Plate Glass Industries, and Koppers Chemical Co. account for 65-70% of the polyester production. It is recommended that these companies be contacted regarding their interest. *It is further suggested that* such a contract be pursued with PPG since they are the manufacturer of RS 50129 and the recommended resin, SR 3704.

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SECTION VIII

MISCELLANEOUS

A. PROMOTER STORAGE

Promoter solution was prepared and tested periodically for reactivity. The resulting gel times for 1.0 phr CHP:0.25 phr promoter were:

Time	Initial	1 day	1 week	2 weeks	21 weeks
Gel Time, min.	9.9	8.0	6.9	7.3	7.7

Promoter solution is stable for extended use periods.

B. FLAME PROPAGATION

FRP mats were inclined at 45° and exposed to burning gasoline. The surfaces of both Cadox 40E cured RS 50129 (AMSS system) and CHP cured, stabilized SR 3704 ignited after several minutes and propagated the flame front. After 7 minutes, the burned area of stabilized resin was slightly less than RS 50129.

RS 50129 was reformulated with 24% Derakane 510, stabilized with inhibitor, cured with CHP, and similarly tested for burning characteristics. No flame propagation occurred.

C. COSTS

The inhibitors used were purchased from Pfaltz and Bauer for:

2,4-Dinitrophenol (Techn).	$14.50/2 kg
p-Toluhydroquinone	$13.50/500 g

The chemical cost (1976 Catalog) of the added components is estimated at about 1-2 cents per pound of resin.

D. DENSITY RELATIONS

Densities of the various components of the newly developed formulation in the uncured and cured (including with Fabmat C-4020 matting) states are shown in Table XIV. These data are required to make changes in pump settings for catalyst and promoter due to volumetric differences between the old and new components, compute shrinkage between the uncured and cured resin, and calculate fiberglass content based on the composite density.

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SECTION IX

CONCLUSIONS

1. The resin formulation recommended for 5 year shelf stability at 75°F is:

SR 3704 (190 cps viscosity) plus
400 ppm (0.04%) 2,4-dinitrophenol
200 ppm (0.02%) p-toluhydroquinone

RS 50129 may be an alternate replacement for SR 3704. The chemical cost of the added components is about 1-2 cents per pound of resin.

2. Temperature is a critical factor in long term storage. One must minimize the effect of heat. Use only new, white, resin-lined drums, or storage tanks. Store drums in a horizontal position with the bungs covered with resin. The storage area should be selected for maximum cooling - a building, shed, or covered area. Avoid direct sunlight and associated heat fluctuations.

3. A new, reliable catalyst system was developed. The catalyst and promoter are:

catalyst - cumene hydroperoxide

promoter - solution of Vanadium Ten Cem: N,N-dimethyl-p-toluidine (3:2 by volume; 2:1 by weight)

The components are fluid at -25°F and usable in AMSS equipment. Equipment to prepare the promoter solution will be necessary. There is an optimum CHP:vanadium ratio for maximum cure. A fixed catalyst:promoter ratio can be used for all temperatures of application; however, variations in the ratio are permissible. Reactivity is most dependent upon promoter concentration. Gel time is easily varied between 10 and 30 minutes. Resin was cured at 32°F.

4. A gel retarder based on methyl ethyl ketone peroxide to further control gel time was demonstrated.

5. Flexural and tensile strength of FRP mats made at 40°F, 73°F, and 120°F exceeded contract specifications.

6. Peroxide storage poses a problem. Low temperature storage is technically feasible from our studies, but is not recommended by peroxide manufacturers. Cumene hydroperoxide is safer and more stable than Cadox 40E.

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SECTION X

RECOMMENDATIONS

A stabilized resin and reactive, reliable catalyst system have been developed. Cure of the catalyzed resin at 32°F was easily demonstrated. The catalyst components are stable and fluid at -25°F. It is recommended that studies be extended to temperatures below 40°F and to higher temperatures above 120°F.

The improved reactivity is a unique advantage. Cures under more severe environmental conditions are distinctly feasible. Limiting parameters of moisture and temperature should be studied with reference to catalyst and resin. The object is to establish a catalyst system which is insensitive to moisture.

The following deficiencies with RS 50129 were observed: (1) a flame front formed from burning gasoline will propagate, and (2) the resin rich areas tend to craze, indicating a brittle resin. A resin was formulated from RS 50129 and 24% Derakane 510 which did not propagate a flame front. Further studies to formulate a nonburning, resilient, tougher resin are recommended.

The principle components of the catalyst system have been identified. It is recommended that other compounds to meet the specific needs of expanded performance be studied. Peroxides with longer shelf life are needed.

A common drive mechanism with a fixed catalyst/promoter ratio should be considered as an equipment modification to reduce human error. A single adjustment would be used to change gel time. This equipment design is feasible because CHP and promoter are uniquely used at a fixed ratio.

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SECTION XI

APPENDIX

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TABLE XII

SHELF STABILIZATION OF RESINS

Sample	Resin	Stabilizer				Time in Hours at:			
		Cpd A	ppm	Cpd B	ppm	120°C	100°C	80°C	50°C
1	RS 50129(PH)	None, as received					4.0		168(288)432
2	"	Solvent (~0.4%)					4.0		
3	"	THQ	300	---	---		9.5		
4	"	ONP	"	---	---		6.0		
5	"	DN	"	---	---		12.5		
6	"	TBHQ	"	---	---		10.5		
7	"	DN	600	---	---	5.3	26.5	144	
8	"	"	1000	---	---		33	195	
9	"	THQ	600	---	---	3.5			
10	"	"	1000	---	---		32	62	
11	"	DN	600	THQ	300		30		
12	"	"	1000	"	"		43		
13	"	"	100	"	"		17	62	
14	"	"	300	"	"		25	144	
15	"	"	600	"	"		43		
16	"	"	1000	"	"		52		
17	"	"	"	"	1000		56		
18	"	"	1500	"	1500	11.8			
19	"	DNP	150	"	450	6.8			
20	"	"	300	"	300	8.3			
21	"	"	450	"	150	9.3			
22	"	"	600	"	---	<8.0			
23	"	DNOC	150	"	450	6.3			
24	"	"	300	"	300	7.8			
25	"	"	450	"	150	8.8			
26	"	"	600	"	---	7.3			
27	"	TBC	150	"	450	4.3			
28	"	"	300	"	300	3.0			
29	"	"	450	"	150	3.0			
30	"	"	600	"	---	1.3			
31	"	PA	150	"	450	6.5			
32	"	"	300	"	300	7.3			
33	"	"	450	"	150	5.8			
34	"	"	600	"	---	3.8			
35	Primary[a]	as Formulated					9.0		
36	"	Solvent (~0.4%)					9.0		
37	"	THQ	300	---	---		10.0		
38	"	ONP	"	---	---		10.0		
39	"	TBHQ	"	---	---		10.0		
40	"	DN	300	---	---		15.5		
41	"	DN	600	---	---		15.5	172	
42	"	"	1000	---	---		26.0	219	
43	"	"	1500	THQ	1500	12.3			
44	"	PA	100	---	---	2.8			
45	"	"	300	---	---	4.3			

[a]Kirtland AFB Primary Resin, 300 ppm THQ (lab bottle age 2 1/2 yrs.)

TABLE XII (continued)

Sample	Resin	Stabilizer				Time in Hours at:			
		Cpd A	ppm	Cpd B	ppm	120°C	100°C	80°C	50°C
46	Primary	PA	600	---	---	5.3			
47	"	"	1000	---	---	6.8			
48	Altek 38-60	As received				2.8			
49	" 38-60M	"	"			3.5			
50	SR 3703[b]	"	"			1.3(1.6)		22	398
51	SR 3704	"	"			1.8		29	504
52	SR 3705	"	"			2.0		>56<72	
53	SR 3706	"	"			3.0		>56<72	
54	SR 3707	"	"			3.0		>56<72	
55	SR 3703	DN	400	THQ	200	11.3		300	
56	"	"	1000	"	300	14.0		350	
57	"								
58	"	---	---	"	600	5.0		<112	
59	"	DN	150	"	450	7.0		180	3960
60	"	"	300	"	300	9.3		248	5616[c]
61	"	"	450	"	150	9.3		264	5664
62	"	"	600	"	---	7.3		176	
63	"	"	150	"	150	5.8		144	
64	"	"	500	"	500	11.7		300	
65	"	"	250	"	250	6.0			3120
66	"	"	400	"	200	7.6			3936
67	"	"	313	"	157	6.8			3312
68	"	"	267	"	133	6.0			2640
69	"	"	243	"	122	5.5			2424
70	"	DNP	200	"	100	6.0		188	
71	"	"	300	"	150	8.0		264	
72	"	"	400	"	200	11.3		312	
73	SR 3704	---	---	"	300	3.5			
74	"	---	---	"	450	4.8			
75	"	---	---	"	600				
76	"	DNP	100	---	---	4.0			
77	"	"	300	---	---	6.8			
78	"	"	450	---	---	7.8			
79	"	"	600	---	---	9.0			
80	"	"	200	THQ	100	8.0		188	
81	"	"	300	"	150	10.0		264	
82	"	"	400	"	200	11.5		312	6192[d]
83	SR 3706	DNP	100	"		2.8			816[e]
84	"	"	400	"	200	8.8		248	4896

[b]SR 3703 (RS 50129 from P.P.G. Labs)

[c]>10,000 cps (75°F) at 5328 hrs.

[d]Fluid at 3864 hrs.

[e]About 8000 cps (75°F) at 3864 hrs.

TABLE XIII

CATALYST STUDIES

Sample	Resin System	Purpose of Test	Catalyst, phr CHP	V	DMT	DDM	Reactivity Gel Time, min.	Exotherm ΔT°C/min.	Hardness Barcol #934
1	RS 50129(PH)	Control	1.0	0.6	Prom.K[a]	---	0.5	Too fast to record	40-44/39-44
2	"		0.33	0.2	"	---	2.5	138/4.4	39-44/40-43
3	"	Effect of DDM	"	"	"	0.5	31.0	5/64	None
4	"	"	"	"	"	0.2	22.5	0/95	None
5	"	"	1.0	"	"	"	3.9	130/11	33-40/33-36
6	"	Effect of DDM[b]	"	"	"	"	1.8	139/6.4	Hard/Cracked
7	"	Effect of DDM	0.5	0.3	"	0.5	8.4	6/22	None
			Stabilized						
8	RS 50129(PH)	600 ppm 2:1 DN:THQ	0.5	0.3	Prom.K	0.5	14.8	76/175	41-45/41-44
9	"		1.0	0.6	"	---	2.4	129/3.7	45/32-35
10	"	400 ppm 2:1 DN:THQ	1.0	0.6	"	---	1.5	138/2.6	43/35-41
11	"	365 ppm 2:1 DN:THQ	"	"	"	---	1.4	"	41-47/39-42
12	"	500 ppm 1:1 DN:THQ	"	"	"	---	2.0	143/3.1	39-43/34-39
13	"	470 ppm 2:1 DN:THQ	"	"	"	---	1.7	130/1.7	41-47/37-44
14	"	"	0.33	6.2	"	---	11.4	103/26	36-41/21-24
		Stabilized RS 50129 containing 24% Derakane 510[c]							
15	RS 50129(PH) with 24% Derakane 510	600 ppm 2:1 DN:THQ	1.0	0.6	Prom.K	---	2.9	128/4.4	38-39/27-33
16	Same at Spl. 15	"	"	"	"	0.2	12.3	125/15	38-39/25
17	"	"	"	"	"	0.3	29.9	125/36	33-40/33-39
18	"	"	"	0.2	"	---	21.3	58/54	37-38/33
19	"	"	0.33	"	"	---	27.2	53/89	34-37/22

[a]Prom. K, Kirtland AFB, 1.8:1.2 V Ten Cem (5%V):DMT, by volume

[b]Fresh DDM, newly received

[c]RS 50129(PH) modified with a brominated resin for reduced flammability

Table XIII (continued)

Sample	Resin System	Purpose of Test	Catalyst, phr CHP	V	DMT	DDM	Reactivity Gel Time, min.	Exotherm ΔT°C/min.	Hardness Barcol #934
20	RS 50129 (PH) Containing 600ppm Stabilizer	1:1 PA:THQ	1.0	0.6	Prom.K	0.3	12.2	134/14	42-46/34-41
21	Same as Spl. 20	3:1 DNP:THQ	"	"	"	"	28.1	128/32	38-42/32-40
22	"	3:1 DNOC:THQ	"	"	"	"	32.9	117/37	42-47/39-43
23	"	DNP	"	"	"	"	30.8	121/41	41-45/31-40
24	"	DN	"	"	"	"	26.5	126/33	35-45/30-35
25	"	THQ	"	"	"	"	12.1	128/14	38-42/33-40
26	"	PA	"	"	"	"	9.1	107/13	41-45/25-30
27	"	DNOC	"	"	"	"	25.8	115/33	36-40/26-33
28	"	DNP[d]	1.0[d]	"	"	0.3[d]	27.1	136/33	40-43/36-42
29	"	PA[d]	1.0[d]	"	"	0.3[d]	8.0	122/18	40-43/22-24
30	"	THQ[d]	1.0[d]	"	"	0.3[d]	15.4	138/17	44-45/33-36
31	"	DN[d]	0.5[d]	"	"	0.15[d]	61.0	112/78	37-41/31-39
32	----	None, Control	0.5	0.3	Prom.K	0.1	7.5	135/12.2	47/41
33	----	"	"	"	"	0.2	12.8	---/>70	36-40/40
34	Same as Spl. 20	2:1 DN:THQ	1.0	0.6	"	0.1	2.7	135/4.2	37-40/30-33
35	"	Vary DDM	"	"	"	0.2	6.3	135/8.2	35-41/20-23
36	"	"	"	"	"	0.3	20.0	129/23.7	36-39/22-28
37	SR 3704	As Received	0.5	0.3	"	None	2.8	146/4.0	40-43/40-43
38	"	"	"	"	"	0.1	9.0	137/11.4	42-45/40-44
39	"	"	"	"	"	0.2	63.4	154/55.2	41/37-43
40	SR 3704 with 600 ppm stabilizer	2:1 DN:THQ	1.0	0.2	"	---	12.0	136/21.4	45-48/43
41	Same as Spl. 40	"	"	0.1	"	---	8.0	4/300	0/10

[d] Catalyst solution - 1.3 phr of a 1:0.3 CHP:DDM solution (DDM added as part of CHP component)

Table XIII (continued)

Sample	Resin System	Purpose of Test	Catalyst, phr CHP	Catalyst, phr Vanadium Promoter	Catalyst, phr DMT	Catalyst, phr DDM	Reactivity Gel Time, min	Reactivity Exotherm ΔT°C/min.	Hardness Barcol #934
				VN-3					
42	SR 3706 + 600 ppm 2:1 DNP:THQ	VN-3 vs. V	1.0	0.3	0.1	---	10.3	141/16.5	42-46/45
43	Same as Spl. 42	"	"	0.45	"	---	5.5	147/7.7	Hard/Crazed
44	"	"	"	0.15	"	---	73.1	0/0	0/0
				VN-2					
45	Same as Spl. 42	VN-2 vs. V	1.0	0.45	0.1	---	29.4	124/44	45-48/43-46
46	"	"	"	0.90	"	---	28.7	103/64	39-44/39-44
47	"	"	"	0.45	0.2	---	15.9	134/27.6	46-51/41-46
				V Ten Cem					
48	Same as Spl. 42	Control	1.0	0.15	0.1	---	5.9	134/7.9	38-42/37-42
				VN-3					
49	SR 3705 + 600 ppm 2:1 DNP:THQ	VN-3 vs. V	1.0	0.375	0.1	---	5.3	155/8.2	45/43 Crazed
50	Same as Spl. 49	"	"	0.25	"	---	13.0	123/25.2	47-51/44-50
				VN-2					
51	Same as Spl. 49	VN-2 vs. V	1.0	0.45	"	---	27.2	119/57.2	43-46/43-47
52	"	"	"	"	0.2	---	14.3	124/25	45/40 Crazed
53	"	"	"	"	0.3	---	7.2	155/9.2	45/42

Table XIII (continued)

Sample	Resin System	Purpose of Test	Catalyst, phr CHP	VN-2	DMT	DDM	Reactivity Gel Time, Min.	Exotherm ΔT°C/min.	Hardness Barcol #934
54	SR 3704 + 600 ppm 2:1 DNP:THQ	VN-2 vs. V	1.0	0.45	0.2	---	15.8	129/25.6	42-46/38-41
55	SR 3704 + 1000 ppm 2:1 DNP:THQ	"	"	"	"	---	24.8	115/47.1	44-50/40-44
56	SR 3703 + 600 ppm 2:1 DNP:THQ	"	"	"	"	---	15.0	133/25.0	42-49/41-46
57	SR 3703 + 1000 ppm 2:1 DNP:THQ	"	"	"	"	---	24.8	108/50.8	42-50/41-45
58	SR 3704 + 600 ppm 2:1 DNP:THQ	"	"	"	0.3	---	10.5	146/15.1	Hard/Crazed
59	Same at Spl. 58	"	"	"	0.1	---	29.1	111/60	45-50/44-49
60	"	"	"	0.23	0.2	---	16.4	139/24.6	Hard/Crazed
61	"	"	"	0.9	"	---	26.0	111/61.7	45/44-46
62	"	"	"	"	"	---	26.3	(Repeated due to long gel time)	
63	"	"	0.5	0.45	"	---	33.5	106/66.2	44-47/42-45
64	"	"	1.5	0.45	"	---	12.8	141/18.9	Hard/Crazed
				V Ten Cem					
65	Same as Spl. 58	"	0.5	0.15	0.10	---	12.4	129/24.9	46/48-50
				VN-2					
66	SR 3703	Production RS 50129 (Oct. 1976)	1.0	0.45[e]	0.1	---	23.5	---	42-45/38-42
67	"	"	"	0.45[f]	"	---	"	---	42-47/37-41

[e] Fresh sample of VN-2, received Sept. 1976

[f] Old sample of VN-2 , received Sept. 1972.

Table XIII (continued)

Sample	Resin System	Purpose of Test	Catalyst, phr CHP	VN-2	DMT	DDM	Reactivity Gel Time, min.	Exotherm, $\Delta T°C$/min.	Hardness Barcol #934
68	SR 3704 + 600 ppm 2:1 DNP:THQ	From Production RS 50129 (Oct. 1976)	1.0	0.65[g] Prom.VN-2			19.0	132/28	45-48/40
69	Same as Spl. 68	"	"	1.30[g]	"	---	14.9	129/23.3	44-46/35-38
70	"	"	2.0	"[g]	"	---	8.1	140/11.9	Hard/Crazed
71	"	"	1.0	0.65[h]	"	---	19.8	125/29.8	---
72	"	"	1.0	0.3	0.2	---	13.9	144/19.4	Hard/Crazed
73	"	"	"	0.2	0.2	---	15.2	142/22.4	"
74	"	"	"	0.1	"	---	36.9	115/77.4	41-45/43-47
75	"	"	"	0.15	"	---	18.7	124/32.2	Hard/Crazed
76	"	"	"	0.25	"	---	15.5	134/23.9	"
77	"	Control with V Ten Cem	"	0.25 Prom.PH[i]		---	7.7	138/14.8	Hard
				VN-2 at 40°F					
78	Same as Spl. 68	"	2.66	0.80	0.53	---	35.0	---	42-46
79	"	"	3.99	1.20	0.80	---	21.9	---	Hard/Crazed 28-30
				V					
80	SR 3704 + 1000 ppm 2:1 DNP:THQ	120°F cure, at 1000 ppm	0.5	0.075	0.05	0.25	25.6	---	---
81	Same as Spl. 80	"	"	"	"	---	12.4	---	---
82	"	40°F cure,at 1000 ppm	2.0	0.3	0.2	---	38.0	---	---
83	"	"	2.5	.375	.25	---	30.3	---	---
84	"	"	3.0	"	"	---	26.3	---	---
85	"	"	3.0	0.375	0.3	---	22.4	---	---

[g] Prom. VN-2 - Soln. of VN-2:DMT 0.45:0.20, by volume

[h] Aged Prom. VN-2 for 24 hrs.

[i] Promoter PH is 3:2 V Ten Cem:DMT (by volume)

Table XIII (continued)

Sample	Resin System	Purpose of Test	Catalyst, phr CHP	V	DMT	DDM	Reactivity Gel Time, min.	Exotherm T°C/min.	Hardness Barcol #934
		2:1 DNP:THQ							
86	SR 3704	600 ppm	1.0	0.25	Prom. (PH)[j]	---	7.2	140/12.4	43-45/42-45
87	"	1000 ppm	"	"		---	10.9	124/23.6	42-45/44-47
88	SR 3703	600 ppm	"	"		---	6.6	144/12.5	43-46/38-43
89	"	1000 ppm	"	"		---	10.4	126/22.1	41-46/40-42
90	SR 3704	600 ppm	"	"		---	6.5	146/11.2	41-45/37-40
91	"	1000 ppm	"	0.15	0.10	---	13.5	128/25.1	43-46/39-43
92	SR 3704 (as recd) on "neat" resin	Reactivity at 32°F	2.0	1.2	Prom. K[j]	---	2.0	(175)/3	Hard/Crazed
93	Same as Spl. 92	"	"	"	"	0.15	8.5	(175)/11.5	"
94	"	"	"	"	"	0.3	10.0	(175)/15.1	"
95	"	"	1.0	0.6	"	----	5.2	177/10.6	" - less
96	"	"	"	"	"	0.15	55	174/81.6	" - "
			DDM/CoN Catalysis						
			DDM	CoN	BPO				
97	RS 50129 (PH)	CoN Catalysis	1.0	1.0	0.5		8.9	106/32	32-38/25-32
			DDM	CoN	DMA				
98	SR 3704 + 600 ppm 2:1 DNP:THQ	"	2.0	0.5	0.2		21.4	-/38	----

[j] Prom. (PH) 3:2 V Ten Cem:DMT; Prom. K, 1:3 V Ten Cem:DMT (by volume)

TABLE XIV

DENSITIES OF COMPOSITIONS

Composition	Density, gram/cubic centimeter
Stabilized SR 3704	
Uncured	1.093
Cured	1.195
C-4020 Composite	1.533 (41.3% glass)
Cumene Hydroperoxide	1.05
Vanadium Ten Cem	1.05
Dimethyltoluidine	0.935 (Mobay)
Glass fibers	2.54